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Application of volume-retarded osmosis and low-pressure membrane hybrid process for water reclamation

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Abstract

A new concept of volume-retarded osmosis and low-pressure membrane (VRO-LPM) hybrid process was developed and evaluated for the first time in this study. Commercially available forward osmosis (FO) and ultrafiltration (UF) membranes were employed in a VRO-LPM hybrid process to overcome energy limitations of draw solution (DS) regeneration and production of permeate in the FO process. To evaluate its feasibility as a water reclamation process, and to optimize the operational conditions, cross-flow FO and dead-end mode UF processes were individually evaluated. For the FO process, a DS concentration of $0.15 \text{ g}\cdot\text{mL}^{-1}$ of polysulfonate styrene (PSS) was determined to be optimal, having a high flux with a low reverse salt flux. The UF membrane with a molecular weight cut-off of 1 kDa was chosen for its high PSS rejection in the LPM process. As a single process, UF (LPM) exhibited a higher flux than FO, but this could be controlled by adjusting the effective membrane area of the FO and UF membranes in the VRO-LPM system. The VRO-LPM hybrid process only required a circulation pump for the FO process. This led to a decrease in the specific energy consumption of the VRO-LPM process for potable water production, that was similar to the single FO process. Therefore, the newly developed VRO-LPM hybrid process, with an appropriate DS selection, can be used as an energy efficient water production method, and can outperform conventional water reclamation processes.

Keywords: Forward osmosis; Hybrid process; Low energy; Low pressure membrane; Volume retarded osmosis; Water reclamation.

1. Introduction

Membrane technology is currently considered to be the most promising alternative for conventional water treatment technologies [1]. This is because membrane technology has a shorter treatment time, higher rejection rate, and more economical values (smaller footprint requirement, and easier operation) than conventional methods [2, 3]. Various types of membrane technologies are recently being used in water and wastewater treatment [4-7].

Of all the membrane processes, the forward osmosis (FO) process has gained increasing attention in the areas of industrial water treatment and desalination, because its operating force is different from that of the pressure-driven membrane process. The FO process is driven by the natural osmotic pressure difference between the feed solution (FS) and the draw solution (DS), and can, therefore, be operated without additional hydraulic pressure. The FO process can remove a wide range of pollutants, and has a lower fouling propensity, higher reversibility, and lower chemical cleaning frequency than a pressure-driven membrane process [8-10]. However, FO processes have their own inevitable drawbacks, such as membrane fouling, DS regeneration, concentration polarization (CP) phenomenon, and short membrane life [11-13]. These drawbacks have a direct impact on the capital expenditure (CAPEX) and operating expenditure (OPEX) of the FO process [14-16]. The most relevant problem regarding cost and energy in the FO process is the limitation of the DS, which is essential for the FO process. Numerous studies have been conducted to find an appropriate DS, as well as to overcome the DS regeneration problem. Recent research on DS has focused on the synthesis of DS using various new materials, or applying a DS that does not need to be regenerated (i.e., fertilizer and seawater) [17-20]. A further research area is that of hybrid technologies, which produce energy or utilize natural energy sources, such as solar heat, tidal power, wind, or geothermal heat to increase energy efficiency in the membrane process [16, 21-23]. However, these have limitations for immediate industry-scale applications, as they require additional technology or are

still under development [24, 25].

In this regard, a volume-retarded osmosis (VRO) and low-pressure membrane (LPM) hybrid process (VRO-LPM) has recently been developed by our research group. This concept originated from the principle of the pressure-retarded osmosis (PRO) process, that generated electricity as the DS volume increased. In both the VRO and PRO (or even FO) processes, the permeate moves from the FS side (low concentration) to the DS side (high concentration) owing to the difference in osmotic pressure, and the volume of the DS increases due to the migrating permeate [26-28]. In the PRO process, however, high-pressure pumps are required to meet the minimum energy requirement for converting the potential energy generated by the increased DS to electrical energy, which is the first point of difference from the VRO-LPM process. In the case of VRO-LPM, the increased DS volume, resulting from the FO process, increases the inner pressure of the closed DS tank, and is a driving force for the LPM part of this hybrid process. Therefore, the main aim of the VRO-LPM process is to minimize the energy consumption of the water treatment process that is typically required in the LPM process to produce final permeate and regenerate the DS. In addition, because the inner pressure is being used directly, the required installation area for the FO-LPM is smaller than for typical FO hybrid systems (i.e., FO-nanofiltration (NF), FO-reverse osmosis (RO)). The two processes (FO and NF) are typically driven separately in the FO-NF process. In this case, operation and maintenance are complex, and continuous cleaning (both physical and chemical) is also required for both membrane processes. However, the VRO-LPM process only uses the principle of the FO process, which makes the system both simpler and cheaper than other hybrid processes, while also being attractive for application in developing countries.

To develop the VRO-LPM hybrid process, two conditions need to be satisfied to make it fully operational. First, because the DS must be filtered with high rejection by the LPM, a polymeric DS is recommended. The polymeric DS must satisfy the following criteria: i) non toxicity; ii) high

solubility; iii) low viscosity; iv) low cost; v) high reusability; vi) low reverse salt (or solute) flux (RSF); and vii) high osmotic pressure in the solution phase [29, 30]. Secondly, the water flux of the FO process is relatively higher than that of the LPM process to maintain an appropriate internal pressure of the DS tank and meet the mass balance.

The main objective of this study was, therefore, to evaluate the feasibility and applicability of the VRO-LPM hybrid process, an energy saving water reclamation process. Three experimental steps (evaluation, modeling, and application) were performed. First, the individual performances of the FO and LPM processes were evaluated as inputs for the design of a VRO-LPM hybrid process. During the evaluation, different concentrations of DS and molecular weight cut-off (MWCO) of the LPM, RSF, of FO processes, and solute rejection of the LPM process were considered. Secondly, a mass balance modeling based on the database obtained from the individual membrane tests, was conducted to study the possibility and feasibility of the VRO-LPM hybrid process. Lastly, the performance of the VRO-LPM hybrid process was tested in the treatment of real secondary wastewater effluent (SWWE).

2. Materials and methods

2.1 Experimental setup

To evaluate the performance of single FO and LPM processes and the VRO-LPM hybrid process, three different experimental setups were required (Figure 1).

2.1.1 Single FO process

First, an FO process was used to evaluate the performance of the single FO process (Figure 1a). A single FO process comprises FS and DS tanks, two gear pumps, a customized cross-flow FO cell (7.7 cm long, 2.6 cm wide, and 0.3 cm deep), and a chiller (CPT Inc., Korea). A digital balance (Sartorius,

ED623S, Goettingen, Germany) was installed under the DS tank to calculate the flux values by measuring the increase in DS weight. The effective membrane area was 20.02 cm². The flow rate and temperature of each solution were fixed at 400 mL·min⁻¹ (cross flow velocity: 8.5 cm·s⁻¹) and 25±1 °C, respectively. The process was conducted in FO mode (active layer facing the FS), and the initial volume of each solution was 1 L. To evaluate the performance in terms of water flux (J_w , L·m⁻²·h⁻¹ (LMH)), the following equation was used.

$$J_w = \frac{\Delta V}{A \Delta t} \quad (1)$$

where, ΔV is the weight change, Δt is the time interval, and A is the effective membrane area. RSF (J_s , g·m⁻²·h⁻¹ (GMH)), was determined by converting the conductivity and total organic carbon (TOC) values of PSS by using Eq. (2).

$$J_s = \frac{\Delta(C_t V_t)}{A \Delta t} \quad (2)$$

where C_t and V_t are the reverse solute concentration and FS volume, respectively, at time t .

Conductivity was measured using a conductivity meter (Orion 4 Star, Thermo Scientific, USA), and the TOC concentration was determined using a TOC analyzer (TOC-L, Shimadzu, Japan).

2.1.2 Single LPM process

The laboratory-scale LPM process is shown in Figure 1b. An Amicon cell used in previous research [31] was used for the LPM process. The experiment was operated in dead-end filtration mode, with a constant nitrogen gas pressure of 5 bar. The pressure was monitored using a digital pressure transmitter (Omegadyne Inc., Model PX319-050G5V, Sunbury, OH). The effective membrane area of the LPM was 32 cm². During the LPM experiment, the amount of permeate was measured using the digital balance. The experiment was terminated when the permeate volume reached 100 mL (the initial FS volume was 300 mL). To investigate the performance (in terms of

solute rejection) of the LPM process, the following equation was used (Eq. (1) was also used to calculate the water flux for the LPM).

$$R = \left(1 - \frac{C_p}{C_F}\right) \times 100 \quad (3)$$

where R (%) is solute rejection efficiency, C_p ($\text{g}\cdot\text{L}^{-1}$) is the solute concentration of the permeate water, and C_F ($\text{g}\cdot\text{L}^{-1}$) is the FS solute concentration.

2.1.3 VRO-LPM hybrid process

The performance of the VRO-LPM hybrid process was evaluated using a designed laboratory-scale VRO-LPM hybrid system. The VRO-LPM system comprised two components (Figure 1c). The first was the FO part, that had only one flow system on the FS side, using a gear pump (Longer Pump WT3000-1FA), with a 70 cm^2 effective membrane area. This is because the VRO-LPM hybrid process operates with the DS tank internal pressure, generated by the permeate volume increasing from the FS of the FO. The second component was the LPM part. The dead-end mode was applied in the LPM part; however, unlike the normal LPM system process, a pressure pump was not required, as the driving force is the increased internal pressure in a closed DS tank from FO permeation. The effective area of the LPM was 32 cm^2 , and the DS tank volume was 800 mL (11 cm wide, 12.5 cm long, and 6 cm high). A magnetic bar was placed on the bottom of the DS tank to minimize the effect of CP on both membrane surfaces (the support layer of the FO membrane and the active layer of the LPM), and to maintain the homogeneity of the DS concentration. A spacer fabricated by a 3D printer (HyVision System, 3DP-210F, Republic of Korea) was installed on the supporting layer of the LPM to prevent the membrane warping from the internal pressure of the DS tank. The water flux of the FO part was obtained by measuring the FS weight decreases with the digital balance. Increases in permeate weight produced from the LPM part were measured by the digital balance, and used to calculate the water flux of the LPM.

Fig. 1. (a) Single FO process, (b) Single LPM process, and (c) VRO-LPM hybrid process.

A commercially available FO membrane (Toray Chemical, Republic of Korea) was used for both the single FO and VRO-LPM hybrid experiments. The FO membrane comprised a thin-film composite polyamide supported by polysulfone and polyester, with a membrane thickness less than 200 μm . The structural parameter ($254 \text{ e}^{-6} \cdot \text{m}^{-1}$) was determined by following a protocol proposed in a previous study [32]. For the LPM (ultrafiltration (UF)) experiment, Amicon YM series membranes

(YM1 and YM3) with different MWCO values were used. The membranes were cut into pieces based on the dimensions of the FO, LPM, and VRO-LPM cells, and were soaked in deionized (DI) water for at least 6 h prior to use.

All experimental conditions were selected based on the FO and LPM tests (sections 2.1.1 and 2.1.2, respectively) to evaluate the first operation of the VRO-LPM under typical operating conditions. However, the performance of the VRO-LPM system should be evaluated in future studies. at different experimental conditions, for further optimization.

2.2 Feed solution (FS) and Draw solution (DS)

DI water was used as the FS for both the single FO and the VRO-LPM hybrid processes. Different concentrations of polysulfonate styrene-sodium (PSS-Na) solution were used as the FS for the single LPM process, and the DS for the single FO and VRO-FO hybrid processes. Laboratory-grade PSS-Na (average molecular weight (MW) $70,000 \text{ g}\cdot\text{mol}^{-1}$) was purchased from Sigma-Aldrich Co. (Germany). The diffusion coefficient of the PSS solution is $280 \times 10^{-6} \text{ m}^2\cdot\text{s}^{-1}$ [33]. More detailed information is presented in section 3.1. To evaluate the feasibility of the VRO-FO hybrid system for water reclamation treatment, SWWE from a wastewater treatment plant (WWTP) in Suwon, Korea, was used as the FS. The SWWE treatment sequence was primary settling, biological treatment, and secondary settling.

2.3 Analytical methods

To determine the characteristics of the SWWE, ultraviolet (UV) absorbance at 254 nm wavelength (UV_{254}) was measured using a spectrophotometer (DR 6000, HACH, USA). A fluorescence spectrophotometer (Shimadzu, Spectrofluorophotometer RF-5301pc, Japan) was used to identify the fluorescence properties of the organic components. In addition, the specific UV absorbance (SUVA) value was obtained from the TOC and UV absorbance values. To determine the inorganic matter in

the FS, an ion chromatography system (ICS-90 and DX 120, Dionex, Sunnyvale, CA, USA) equipped with IonPac AS14 and CS12A columns (Dionex, Sunnyvale, CA, USA), and an inductively coupled plasma-mass spectrometer (ICP-MS) (7500ce, Agilent, Santa Clara, CA, USA) were used. The osmotic pressure of the DS was measured by a freezing point osmometer (Fisk® Micro-Osmometer Model 210, USA). To analyze the viscosity, polarity, and particle size of the PSS-Na solution, a Viscometer (Vibro viscometer SV-1A, A&D weighing, USA), and zeta potential analyzer (Nanotrac Wave II, Microtrac, USA) were used, respectively.

2.4 Mass balance modeling of VRO-LPM process

The simulation model for a VRO-LPM hybrid process was developed by combining the water permeate flux equations of the FO/PRO mode and the LPM process, as shown in Eqs. (4) and (5), respectively.

2.4.1 Water permeate flux and water production

The water permeate flux of the FO/PRO mode was taken as the dilutive internal concentration polarization (ICP) [LMH] (Figure A.1).

$$J_{FO/PRO} = A(\pi_{D,b} \exp(-J_{FO/PRO} K) - \pi_{F,b} \exp(\frac{J_{FO/PRO}}{k}) - \Delta P) \quad (4)$$

where A is the pure water permeability coefficient, $\pi_{D,b}$ and $\pi_{F,b}$ are the bulk osmotic pressures at the draw and feed sides, respectively, $J_{FO/PRO}$ is the water permeate flux of the FO/PRO mode, $K = \frac{t\tau}{D_s \varepsilon}$, τ is the tortuosity, t is the membrane thickness, ε is the porosity, k is the mass transfer coefficient that can be calculated by the Sherwood number [34], and ΔP is the applied pressure in the DS.

The water production of the FO/PRO mode was calculated as follows.

$$W_p = A_{FO/PRO} J_{FO/PRO} \quad (5)$$

where W_p is the water production and $A_{FO/PRO}$ is the effective area of the membrane.

In the proposed VRO-LPM hybrid process, the DS pressure difference was not zero-based in the design process. Typically, the pressure difference on the DS side is zero in the FO mode. Therefore, this process can be regarded as the PRO mode, and ΔP in Eq. (4) is generated from the draw tank volume by increasing the water permeate flux of the PRO mode.

2.4.2 LPM equation

The general equation of water production for the LPM process is expressed by Eq. (6).

$$J_{UF} = \frac{\Delta P}{R_{ult_m}} \quad (6)$$

where A_{LPM} is the effective area of the LPM membrane, ΔP is the applied pressure in the DS, and R_{ult_m} is the LPM membrane resistance coefficient.

The LPM water production is calculated by Eq. (7).

$$W_p = A_{UF} J_{UF} \quad (7)$$

In the VRO-LPM hybrid process, the water is produced in series across the processes. Overall water production is estimated by Eq. (8).

$$W_p = A_{FO/PRO} J_{FO/PRO} = A_{UF} J_{UF} \quad (8)$$

Combining Eqs. (4)–(8) yields

$$W_p = A_{\frac{FO}{PRO}} A(\pi_{D,b} \exp\left(-J_{\frac{RO}{PRO}} K\right) - \pi_{F,b} \exp\left(\frac{J_{\frac{FO}{PRO}}}{k}\right) - \Delta P) = A_{UF} = \frac{\Delta P}{R_{ult_m}} \quad (9)$$

In the proposed VRO-LPM hybrid process $J_{FO/PRO}$ and J_{LPM} are linked by ΔP . Therefore, Eqs. (4)–

(7) were calculated iteratively as per Broyden's method to satisfy Eq. (8), namely the mass balance equation.

3. Results and Discussion

3.1 Polysulfonate styrene-sodium

To evaluate the suitability of PSS-Na as the DS, physico-chemical analyses, such as conductivity, osmotic pressure, viscosity, zeta potential, and TOC at different PSS-Na concentrations, were conducted before the single FO and LPM experiments.

The physico-chemical properties of the DS are critical factors in osmotic driven membrane processes [18, 35, 36]. The characteristics of the PSS-Na (DS) according to its concentration are presented in Table 1. The conductivity and osmotic pressure of PSS-Na DS increase proportionally with increasing PSS-Na concentrations, which indicates that a PSS-Na DS has sufficiently large ionic strength to generate enough osmotic pressure for the FO process. Typically, high conductivity and osmotic pressure result in high water flux and RSF. The TOC value of a PSS-Na DS also increases linearly with increasing PSS-Na DS concentration. However, the viscosity increased when the PSS-Na DS concentration increased. It is known that a high viscosity leads to a significant CP phenomenon, causing a decline in water flux [18, 37]. In addition, PSS-NA has a high negative polarity in the solution phase, which can reduce the RSF caused by concentration differences across the membrane (high concentration side to low concentration side) [9, 38, 39]. Therefore, it is necessary to determine the optimal PSS-Na DS concentration. The PSS-Na DS charge became more negative with increasing PSS-Na DS concentrations. The PSS-Na solution is obtained by dissolving the PSS-Na into DI water. Once the PSS-Na is dissolved, PSS and Na are dissociated and become ions, making PSS an anion. The number of charged PSS ions increases as the concentration increases, and this increases the negativity of the PSS, as can be seen in Table 1. As the concentration increased,

the negativity and osmotic pressure increased, indicating that the number of anions also increased. The electrostatic repulsive force generated between the FO membrane surface, having a negative charge, and the PSS ions is strongly induced. Therefore, the negativity of the PSS ions is expected to have a positive effect on the FO performance [17, 37].

Table 1. PSS-Na draw solute physico-chemical characteristics.

Concentration (g·mL ⁻¹)	Conductivity (ms·cm ⁻¹)	Osmotic pressure (bar)	Viscosity (mPa·s)	Zeta potential (mV)	TOC (mg·L ⁻¹)
0.04	8.5	3.2	3.3	-79.8	16.9
0.08	17.6	5.2	5.3	-81.5	32.4
0.10	21.3	8.9	6.3	-177.5	46.5
0.15	27.6	12.0	10.8	-199.2	52.5
0.22	40.8	16.7	21.6	-216.7	66.1

3.2 Performances of single FO and LPM processes

3.2.1 Single FO process

Figure 2 shows the initial water flux and RSF (on average) of the single FO process at different PSS-Na DS concentrations, ranging from 0.04–0.22 g·mL⁻¹, during the 4-h experiment. It can be seen that the PSS-Na DS concentration affected the water flux and RSF, as expected. As the PSS-Na DS concentration increased, the water flux also increased. However, the RSF value also increased with increasing PSS-Na DS concentrations. Interestingly, when the PSS-Na DS concentration increased from 0.08 to 0.10 g·mL⁻¹, the water flux exhibited a significant increase, from 7.5 to 11.3 LMH, and the RSF value increased from 0.22 to 0.52 GMH. According to Table 1, at a concentration

of $0.08 \text{ g}\cdot\text{mL}^{-1}$, the osmotic pressure, viscosity, and polarity were 5.2 bar, $5.3 \text{ mPa}\cdot\text{s}$, and -81.5 mV , respectively. However, when the PSS-Na DS concentration increased to $0.10 \text{ g}\cdot\text{mL}^{-1}$, the osmotic pressure, viscosity, and polarity, respectively increased to 8.9 bar, $6.3 \text{ mPa}\cdot\text{s}$, and -177.5 mV . The proportional increases in osmotic pressure, viscosity, and polarity were approximately 1.70, 1.19, and 1.45, respectively. As mentioned in section 1, for FO processes that use polymers as a DS, viscosity has a dominant effect on the performance [18, 29, 37]. Moreover, the polarity of the solution indirectly exhibited a degree of ionization of the PSS ions in the solution, indicating ion diffusivity and mobility. Therefore, the water flux increased significantly, while the increase in RSF was relatively small compared to the water flux. This could be a result of the effects of electrostatic repulsion between the FO membrane and the PSS ions. The increase in the DS concentration increased the osmotic pressure difference across the membrane, resulting in an improved FO process performance. It is noteworthy that the water flux decreased slightly when the concentration was increased from 0.15 to $0.22 \text{ g}\cdot\text{mL}^{-1}$, while the RSF increased from 0.68 to 0.78 GMH. This could be because of the effects of viscosity and CP. The $0.22 \text{ g}\cdot\text{mL}^{-1}$ PSS-Na DS had a viscosity of $21.6 \text{ mPa}\cdot\text{s}$ and a polarity of -216 mV . Compared to the $0.15 \text{ g}\cdot\text{mL}^{-1}$ PSS-Na DS, the rate of increase of both viscosity and polarity were significant. As mentioned in section 3.1, increased viscosity reduced both ion diffusivity and osmotic pressure. As a result, a significant CP occurred, with the subsequent adverse effect on the FO performance.

Fig. 2. Single FO process water flux and reverse salt flux versus PSS (DS) concentrations.

3.2.2 Single LPM process

Fig. 3. Performances of single LPM: a) water flux, and b) rejection.

Figures 3a and b show water flux and rejection rates, respectively, for two different LPM MWCO values (1 and 3 kDa), at various PSS-Na concentrations. Note that as the VRO-LPM hybrid process simultaneously dilutes and recovers the DS, the concentration of the DS used in the single FO experiment, and that of the FS in the single LPM process, are identical. In addition, the LPM part of VRO-LPM hybrid process, as well as the single LPM experiment, was conducted in a dead-end mode. As can be seen in Figure 3a, the water flux of LPM decreased as the PSS-Na concentration increased, possibly as a result of PSS deposition on the LPM surface and the formation of the CP layer.

However, a smaller MWCO value of LPM corresponded to a higher observed rejection rate (Figure 3b). The rejection rate decreased for 3 kDa with increasing PSS-Na concentrations, while for 1 kDa, there was a marginal increase as the concentrations increased. The highest rejection rate (90%)

was achieved at $0.15 \text{ g}\cdot\text{mL}^{-1}$. For high PSS-Na solution concentrations, the diffusion or convection of the small-sized PSS molecules through the membrane is a result of the concentration difference across the LPM. However, for a lower MWCO LPM value (1 KDa), the small PSS molecules could pass through the LPM, and the rejection rate increases due to the electrostatic repulsion between the negatively charged PSS ions and the negatively charged LPM surface. In general, the removal mechanism of the LPM is classified as sieving by pore size, removal by chemical characteristics of membrane and solution (electrostatic repulsion), and hindrance by back diffusion [40, 41]. From the single LPM experiment using PSS-Na as an FS, it was surmised that rejection by electrostatic repulsion was dominant. However, at a concentration of $0.22 \text{ g}\cdot\text{mL}^{-1}$, the rejection rate was lower than $0.15 \text{ g}\cdot\text{mL}^{-1}$. This is because of the diffusion or convection forces, which are stronger than the electrostatic repulsion force. Therefore, it is necessary to select suitable FO and LPM membranes, and an optimal DS concentration, for high operating efficiency of the VRO-LPM hybrid process. Therefore, modeling studies based on the results of the single FO and LPM experiments should be conducted to determine the optimal operating and designing parameters.

3.3 VRO-LPM hybrid process simulation results

The mass transfer coefficients, as the permeability of the FO/PRO mode and the LPM, were estimated based on the single FO and LPM experiments. In the LPM process, the gel layer resistance was assumed to be zero for simplification of the governing equation (Eq. (9)). In this section, the performance of proposed process was investigated at various osmotic pressure differences, from 3.2 to 16.7 bar. This confirmed that the primary driving force was caused by an osmotic pressure difference between the draw and feed sides on the FO/PRO mode side. Figure 4a shows theoretical (or modelled) water production (as a volume flow rate), and pressure applied in the DS tank according to PSS (in the DS) concentrations, or osmotic pressure changes. The water production of the proposed VRO-LPM hybrid process increased from 0.103 to $0.790 \text{ mL}\cdot\text{h}^{-1}$ as the osmotic

pressure difference increased from 3.2 to 16.7 bar. The predicted pressure difference applied in the DS tank also increased from 2.8 to 7.4 bar as the water production increased. Interestingly, the pressure was the highest at a DS concentration of $0.15 \text{ g}\cdot\text{mL}^{-1}$, at a pressure of 8.3 bar. This was because the difference in water flux between the single FO and LPM processes was the greatest at $0.15 \text{ g}\cdot\text{mL}^{-1}$, as can be seen in Figures 2 and 3a. Compared to the water production of the single experiments, the water production of the VRO-LPM hybrid system was lower. This indicated that the decreased water production was a result of the generated pressures associated with both the LPM and FO processes. As the increased pressure acts against the force generated by the osmotic pressure difference, the overall flux from the FO part of the hybrid process will be reduced, resulting in a smaller permeate volume. However, the generated pressure difference from water production in the DS tank produces the water through the LPM. Therefore, it is evident that the relationship between the fluxes of the FO and the LPM is a trade-off because of their orientation in the VRO process. The optimal fluxes that generate well mass-balanced permeate volumes for both the FO and LPM process within the VRO process were calculated through modelling, and are presented in Figure 4b. According to the modelling results presented in Figures 4a and 4b, it was confirmed that the VRO-LPM has the potential of producing water. The optimal PSS-Na concentration according to the modelling results was $0.15 \text{ g}\cdot\text{mL}^{-1}$; however, this theoretical value is only valid if the effects of the gel layer and the CP are negligible.

Fig. 4. (a) Modelled permeate volume and internal pressure in VRO-LPM hybrid process, and (b) optimum water flux of FO and LPM processes.

3.4 Performance of VRO-LPM hybrid process

Based on the results obtained from the single FO and LPM experiments and modeling studies, the VRO-LPM hybrid process was operated with a PSS concentration of $0.15 \text{ g}\cdot\text{mL}^{-1}$. The performance of the VRO part in the VRO-LPM hybrid process, in terms of water flux and RSF, is shown in Figure 5a, and the performance of the LPM part is shown in Figures. 5b and 5c. With LPM of 1 kDa and 3 kDa in the VRO-LPM hybrid processes, the water fluxes of the VRO part were 6.1 and 6.4 LMH, and the RSFs were 0.10 and 0.16 GMH, respectively. The results were lower than those of the single FO process, where the water flux and RSF values for single FO and VRO-LPM system were 12.1 and 6.4 LMH, and 0.68 and 0.16 GMH, respectively. Because of the VRO-LPM hybrid process characteristics, the LPM process was driven by utilizing the internal pressure of the DS tank by diluting the DS with permeate from the VRO process. Therefore, the internal pressure generated in the DS tank affected the VRO performance. The internal pressure was expected to serve as a factor to increase the RSF; however, the RSF value was significantly reduced (pressure applied from draw side to feed side). This was possibly a result of the VRO-LPM hybrid process that exists in a closed loop system without DS circulation. Therefore, as permeate passed through the membrane, and ICP occurred, the concentration difference across the membrane was reduced. The cross flow-type FO process could reduce the CP phenomenon through turbulence generated by increasing cross flow velocity. Figure 5b shows the calculated pressure generated inside the VRO-LPM hybrid process, based on the amount of permeate actually obtained from the VRO and LPM parts, and the results of the single LPM process. When 1 kDa and 3 kDa LPMs were used for the VRO-LPM hybrid process, 0.23 and $0.18 \text{ mL}\cdot\text{min}^{-1}$ more permeate was generated by the VRO part than by the LPM part, respectively. The water flux of the VRO part was less than that of the LPM part; however, as the effective membrane area of the VRO was approximately twice that of the LPM, the actual amount of permeate generated by the VRO was greater. This resulted in an internal pressure of approximately 8 bar inside the DS tank. The rejection rate of the VRO-LPM hybrid process was 90% and 75% for 1

kDa and 3 kDa LPMs, respectively (Figure 5c). Although the VRO-LPM hybrid process exhibited a lower performance than the single processes, permeate could be produced without a regeneration pump on the LPM side, which is a primary benefit of this process.

At $0.15 \text{ g}\cdot\text{mL}^{-1}$ of PSS-Na DS, the theoretical flux values were 3.7 and 8.0 LMH for the FO and LPM, respectively, but the experimental flux values were 5.8 and 8.4 LMH for the FO and LPM, respectively. In addition, the theoretical internal pressure was 8.4 bar, but the actual pressure was 8.0 bar. With the exception of the water flux values for the FO process, the theoretical values and the experimental results of other parameters were similar. The difference in theoretical and experimental flux values for the FO process could result from the extra force generated by the flow rate of the FS. This extra force exerted from the FS side cancels out the effect of increased internal pressure in the DS tank. Moreover, the modelling was done with the assumptions that the effects of the FS flow rate and CP are negligible. These assumptions resulted in lower FO flux values than the experimental FO flux values. A brief comparison of the performances between the individual processes and the hybrid process was performed. At $0.15 \text{ g}\cdot\text{mL}^{-1}$ of PSS-Na DS, the water flux and RSF for the individual FO process were 12.1 LMH and 0.78 GMH, respectively, and water flux and rejection for the single LPM process were $1.04 \text{ LMH}\cdot\text{bar}^{-1}$ and 91%, respectively. However, in the VRO-LPM system, the FO part had a water flux of 5.8 LMH and RSF of 0.10 GMH, and the LPM part achieved similar water flux and rejection rates to those obtained from the individual LPM process.

Fig. 5. VRO-LPM hybrid system operation: (a) water flux and reverse salt flux of VRO, (b) actual permeate volume and pressure, and c) LPM rejection rate.

3.5 Water reclamation application study

Based on the single FO, LPM, and VRO-LPM hybrid process experiments, the feasibility of the newly developed process was confirmed. In an application study conducted as a final step, simultaneous wastewater treatment of VRO-LPM was evaluated using SWWE as the FS. Typically, FO membranes have high rejection rates of organic matter, inorganic matter, and micro-pollutants allowing high-quality water to be produced [19, 42, 43]. Figure 6 shows the water flux and the amount of permeate produced when the VRO-LPM hybrid process was operated for 12 h with SWWE from the WWTP as the FS. The PSS rejection rate by the 3 KDa LPM was lower than that by the 1 kDa LPM in the VRO-LPM hybrid process (Figure 5c). Therefore, the 1 kDa LPM was selected for this experiment. The water flux and the amount of permeate were observed to be 4.1 and 5.2 LMH, and 0.48 and 0.28 mL·min⁻¹ for the VRO and LPM, respectively. As mentioned in section 3.1.1, it was expected that the SWWE would cause membrane fouling and a significant performance

reduction in the membrane process. However, based on the results, the VRO-LPM hybrid process showed promising performance that can be applied for water reclamation because of its less thick fouling layer, and high fouling reversibility.

Fig. 6. VRO-LPM hybrid process water flux with SWWE.

4. Conclusions

The feasibility of the VRO-LPM hybrid process for water reclamation was successfully demonstrated. A 0.15 g·mL⁻¹ PSS-Na DS achieved not only a large water flux, but also a high rejection rate in single FO and LPM processes, respectively. Water flux of the FO part of the VRO-LPM process was approximately 50% lower than that of the single FO process; however, for the LPM process, the single LPM process and the LPM part of the hybrid process exhibited similar performance. This indicated that an adverse effect of internal pressure in the DS tank occurred during the FO process, but the final product was effectively produced from the LPM process. However, it could be improved by adjusting the effective membrane area by controlling the permeate volume rate. Through modeling and experiments, it was confirmed that the VRO-LPM hybrid process could be

operated without pumps for regenerating the DS and production of the final permeate, resulting in a more energy efficient process when compared to the other processes. To further optimize and commercialize the VRO-LPM system, the selection of a more appropriate DS, including its concentration, should be conducted. More precise information on the pressure conditions for stable mass transfer from the VRO part to the LPM part is also necessary for a practical application of a VRO-LPM system. An economic evaluation, based on specific energy consumption (SEC) values of single and hybrid processes, can be found in Appendix A.

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Highlights

- New energy saving forward osmosis-low pressure membrane hybrid process was tested.
- The system could produce final product with an increase in inner pressure of tank.
- A polymeric draw solute was effective in the operation of this hybrid system.
- A mass balance modeling was used for optimization.
- An applicability of this hybrid process in wastewater treatment was confirmed.